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Experimental studies of the *KLL* Auger spectra of Cu and Ge

By Evelyn Sokolowski and Carl Nordling

With 3 figures in the text

ABSTRACT

The energies of the Auger lines of Cu and Ge, belonging to the *KLL* group, have been determined, and the intensities have been estimated. For both elements, six components could be established in the *KLL* group. The experimental data are in good agreement with the theoretical results of Asaad and Burhop, ref. [4], as regards the relative energies and intensities. The absolute energies deviate by 40 and 50 eV respectively.

Introduction

Contributions to Auger theory in the region of intermediate coupling have been scarce in the last few years. This might be attributed to the fact that little experimental data have been available that might incite renewed theoretical considerations. The experimental difficulties have been the following: *ad primo*, in the region of intermediate coupling, i.e. in the intermediate part of the periodic table, the spacing of the final states is so small, even for *KLL* transitions, that a detailed study requires an instrument of very high resolution. *Ad secundo*, the energy of the *KLL* group is so low that, in order to make an accurate energy determination, one must have a spectrometer of good linearity even in the low energy region. Finally, since in most investigations of Auger spectra, radioactive samples have been employed, there arises the problem of securing sufficient intensity. Lately, the improved techniques of β-ray spectroscopy have helped overcome some of these difficulties, and, recently, new data on the K Auger spectra of some intermediate elements have become available; Bellicard *et al.* [1, 2] have studied the Auger electron emission from radioactive Zn and Co. Sokolowski, Nordling and Siegbahn [3] have reported an investigation of the K Auger spectrum of Cu, in which X-radiation has been used to produce the initial ionization of the K shell. These experimental studies have now been followed by an extensive theoretical treatment of K Auger spectra by Asaad and Burhop [4]. Calculations have been made of the relative transition probabilities in the *KLL* and *KLM* groups, as well as of the transition energies. In the present investigation the *KLL* Auger spectrum of Ge has been studied and that of Cu has been analyzed further in the light of ref. [4].

Experimental procedure and results

The apparatus used was that described in ref. [3]. The source, an evaporated metal layer of about 100 Å thickness, served as a converter for X-radiation, and the resulting electron spectrum was analyzed magnetically by means of an iron-free, double-focussing spectrometer [5]. The detector was a GM-counter with a window cut-off of about 2 keV.

In order to study the general appearance of the lines under the conditions used throughout, the K photo lines of Ge due to Mo $K\alpha$ radiation were recorded (Fig. 1). In ref. [3] the corresponding lines of Cu were studied and found to have the same features: each photo peak is accompanied by one satellite of lower intensity and about 15 eV lower energy. These satellites have been attributed to electrons, scattered inelastically in the source [3]. One might expect a sequence of such satellites, corresponding to different modes of excitation of the electron plasma [6], or due to multiple scattering, and hence, with sufficiently narrow lines, one runs the risk of obtaining a number of "false" peaks in a spectrum. In the Auger spectra of Ge and Cu the natural line width is smaller than for the photo lines by about 50 % of the photo line width, due to the contribution of the Mo Kα line to the latter. With the spectrometer settings usually employed in this investigation, the spectrometer window contributes approximately 50 % of the total width of a photo line. In order to reduce

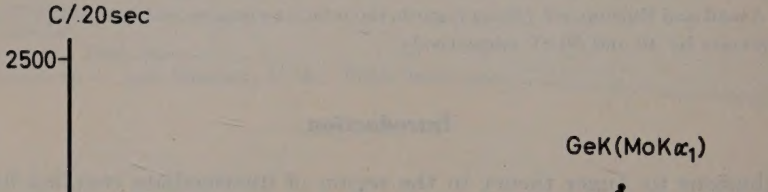

Fig. 1. Photo electron lines of germanium. The electrons are expelled from the K shell in Ge by Mo $K\alpha_1$ and Mo $K\alpha_2$ X-radiation. Only one satellite peak (D.E.L.) due to discrete energy losses on scattering in the source is observed for each photo line. (In the region plotted with filled circles the statistics are twice as good as indicated by the ordinate.)

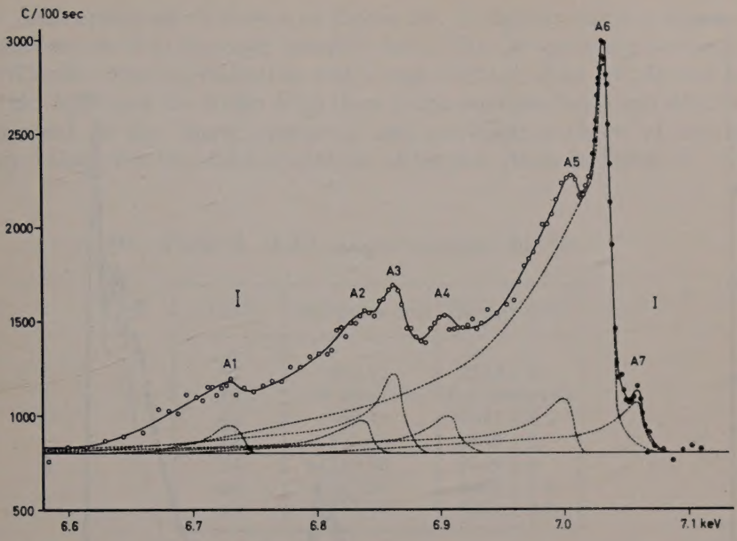

Fig. 2 *a*.

Fig. 2. *KLL*-Auger spectra of (*a*) copper and (*b*) germanium. In the copper spectrum, for which a very thin source was used, the peaks due to inelastically scattered electrons are weak.

the photo line width to the same magnitude as the Auger line width, the spectrometer resolution was increased correspondingly and the low energy flanks of the photo lines were scanned for further satellites. Even then, not more than one satellite was found for each photo peak. As might be expected, the intensity of the satellites was found to be a function of the source thickness.

In all the Cu and some of the Ge runs, the spectrometer was calibrated with the Cu K(Mo $K\alpha_1$) line, the $B\varrho$ value of which was taken to be 312.09 gauss-cm. This value differs from that given in ref. [3] since a correction for a residual magnetic field has been applied [12]. For the Ge measurements a "triple" source holder was used [7], with Ge deposited on the middle section and Cu on the outer sections. The three sections were successively slid into the same position in the X-ray beam. In the cases where Ge was studied with Zr X-radiation, the Cu K(Zr $K\alpha_1$) line was used for the calibration. Its $B\varrho$ value, 278.79 gauss-cm, was obtained from the $B\varrho$ value of the Cu K(Mo $K\alpha_1$) line together with the Mo $K\alpha_1$ and Zr $K\alpha_1$ energies as given by Sandström [8].

The *KLL* Auger spectrum of Cu, already studied in ref. [3], was again recorded in the present investigation (Fig. 2*a*). The exciting X-radiation was that of Mo, with a high voltage of 45 kV. An exceptionally thin source was used, which resulted in weak satellites. Seven lines were found in the spectrum, in agreement with the results of [3]. In the present case an attempt was made to separate these lines graphically, the analysis being based on equal quarter- and halfwidths for the different lines. After the graphical separation of the components the energy values were reconsidered,[1]

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[1] *Erratum.*—In Table 3, ref. [3], giving preliminary B_ϱ- and energy values for the *KLL* Auger lines of Cu, there are errors in the transformation from B_ϱ to energy for two of the lines, namely *A*1 and *A*3.

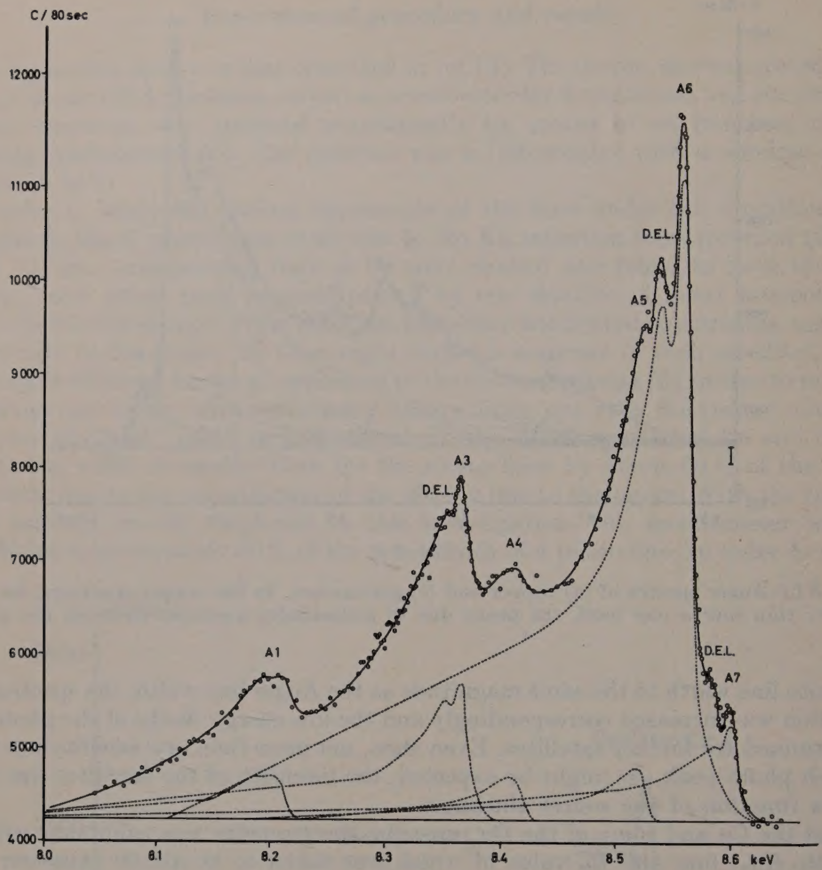

Fig. 2 *b.*

with the sloping background of some of the lines taken into account. For some of the weakest lines, the peak due to unscattered electrons is not clearly distinguishable from the low energy tail, which tends to shift the peaks towards too low an energy. This was corrected for by assigning to all lines the same half-width also for the *high energy* part. The revised $B\varrho$- and energy values for the *KLL* spectrum of Cu are given in Table 1.

Table 1. KLL Auger energies for Cu.

Line	$B\varrho$ (gauss cm)	Energy (eV)
*A*1	277.72	6739 ±6
*A*2	279.74	6836 ±6
*A*3	280.37	6867 ±4
*A*4	281.23	6909 ±6
*A*5	283.21	7006 ±2.5
*A*6	283.79	7034.5 ± 1.0
*A*7	284.38	7063 ±2.5

The Ge *KLL* spectrum is shown in figure 2*b*. A slightly thicker source was used, which manifests itself in stronger satellite lines. The Ge spectrum was recorded with Mo- as well as Zr- and Ag radiation and a high voltage of 45 kV. In the former case the Ge K(Mo $K\beta_1$) and Ge K(Mo $K\beta_3$) lines (with energies 8499 and 8482 eV respectively) appeared in the Auger spectrum and provided a check of the calibration. The energy values for the *KLL* spectrum of Ge are given in Table 2.

Table 2. KLL Auger energies for Ge.

Line	$B\varrho$ (gauss cm)	Energy (eV)
$A1$	306.81	8212 ± 6
$A2$	not observed	not observed
$A3$	309.71	8367 ± 4
$A4$	310.60	8415 ± 6
$A5$	312.63	8524 ± 4
$A6$	313.31	8561 ± 2.5
$A7$	314.04	8601 ± 2.5

Discussion of results

It was stated in ref. [3] that ten lines can be expected in the *KLL* Auger spectrum for intermediate coupling, corresponding to the final states

$$KL_{\mathrm{I}}L_{\mathrm{I}} \quad \cdots\, 2s^0\; 2p^6 \,\cdots \quad {}^1S_0$$

$$\begin{array}{l} KL_{\mathrm{I}}L_{\mathrm{II}} \\ KL_{\mathrm{I}}L_{\mathrm{III}} \end{array} \quad \cdots\, 2s^1\; 2p^5 \,\cdots \left\{ \begin{array}{l} {}^1P_1 \\ {}^3P_2 \\ {}^3P_1 \\ {}^3P_0 \end{array} \right.$$

$$\begin{array}{l} KL_{\mathrm{II}}\,L_{\mathrm{II}} \\ KL_{\mathrm{II}}\,L_{\mathrm{III}} \\ KL_{\mathrm{III}}L_{\mathrm{III}} \end{array} \cdots\, 2s^2\; 2p^4 \,\cdots \left\{ \begin{array}{l} {}^1S_0 \\ {}^1D_2 \\ {}^3P_2 \\ {}^3P_1 \\ {}^3P_0 \end{array} \right.$$

The KL_mL_n notation is appropriate for those cases where the coupling is nearly pure *j-j*, i.e. for high Z. Burhop has pointed out [9] that the transition probability to the ${}^3P_1$ state of the $2s^2 2p^4$ configuration is identically zero and can be disregarded in the theoretical treatment. In ref. [4] the energies and relative intensities of the remaining nine *KLL* transitions have been calculated for various elements with Z ranging between 26 and 83. For the energies a set of general equations is given, which depend on the binding energies of the atomic shells involved and a group of functions, F and G, accounting for the screening and the exchange energy. For these latter functions the authors assume the following dependence on Z:

$$F\,(\text{or } G) = A\,(Z - Z_s)(1 - \alpha Z^2).$$

The sets of constants A, Z_s and α have been evaluated semiempirically for all F and G to fit the experimental data for $Z = 83$ as given by Mladjenovic and Slätis [10]. It may be noted that, for $Z \lesssim 30$, the relativistic factor $(1 - \alpha Z^2)$ is almost negligible, the functions being almost linear with Z. For the atomic binding energies, Asaad and Burhop have used the values given by Hill, Church and Mihelich [11], which are based on X-ray absorption data. These values generally do not include the electronic work functions, which should be subtracted from the energy expressions in ref. [4].

The theoretical intensities quoted below for Cu and Ge were obtained by means of interpolation from Table 1, ref. [4]. Figure 3 gives the *relative* energies and intensities of the *KLL* transitions as obtained theoretically and experimentally. The theoretical lines have been normalized to the $L_{II}L_{III}(^1D_2)$ line and the experimental ones to the *A*6 line. These two lines must be identified with each other for intensity reasons. The agreement between the experimental and the theoretical spectra is so good that the interpretation of the experimental lines is beyond doubt. The data are given in Table 3.

Table 3.

Experimental notation	Theoretical notation	Relative energy (eV)		Relative intensity	
		Exp.	Theor.	Exp.	Theor.
Cu *A*6	$L_{II}L_{III}(^1D_2)$	0	0	100	100
*A*7	$L_{III}L_{III}(^3P_2)$	+ 28	+ 26	13	14
*A*5	$L_{II}L_{II}(^1S_0)$	− 29	− 29	13	7
*A*4	$L_{I}L_{III}(^3P_1)$	− 126	− 124	9	7
*A*3	$L_{I}L_{II}(^1P_1)$	− 168	− 166	22	50
*A*2	—	− 199	—	7	—
*A*1	$L_{I}L_{I}(^1S_0)$	− 296	− 295	7	18
Ge *A*6	$L_{II}L_{III}(^1D_2)$	0	0	100	100
*A*7	$L_{III}L_{III}(^3P_2)$	+ 40	+ 36	14	18
*A*5	$L_{II}L_{II}(^1S_0)$	− 37	− 40	7	7
*A*4	$L_{I}L_{III}(^3P_1)$	− 148	− 146	6	9
*A*3	$L_{I}L_{II}(^1P_1)$	− 194	− 198	23	50
*A*2	—	—	—	—	—
*A*1	$L_{I}L_{I}(^1S_0)$	− 349	− 351	7	18

For the line, denoted by *A*2 in the Cu spectrum, there is no correspondence in the theoretical spectrum or in Ge. Its classification as an Auger line must therefore be reconsidered. In the Cu spectrum, this line cannot very well be interpreted as a satellite due to discrete energy losses, the line being too far away from the stronger *A*3 line. Its origin in Cu was definitely established in ref. [3], where the line was not observed when no Cu had been evaporated onto the source backing.

A comparison between theory and experiment regarding the absolute energies does not give quite as good an agreement. The calculated energies are about 40 and 50 eV too low for Cu and Ge, respectively. This discrepancy must primarily be sought in the functions F and G, to which the absolute energies are more sensitive than the relative values.

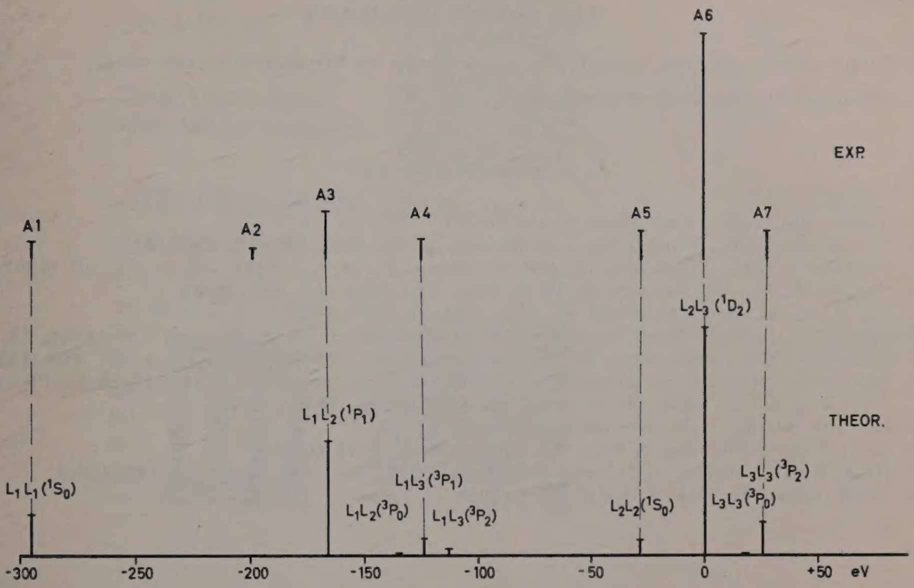

Fig. 3 *a*.

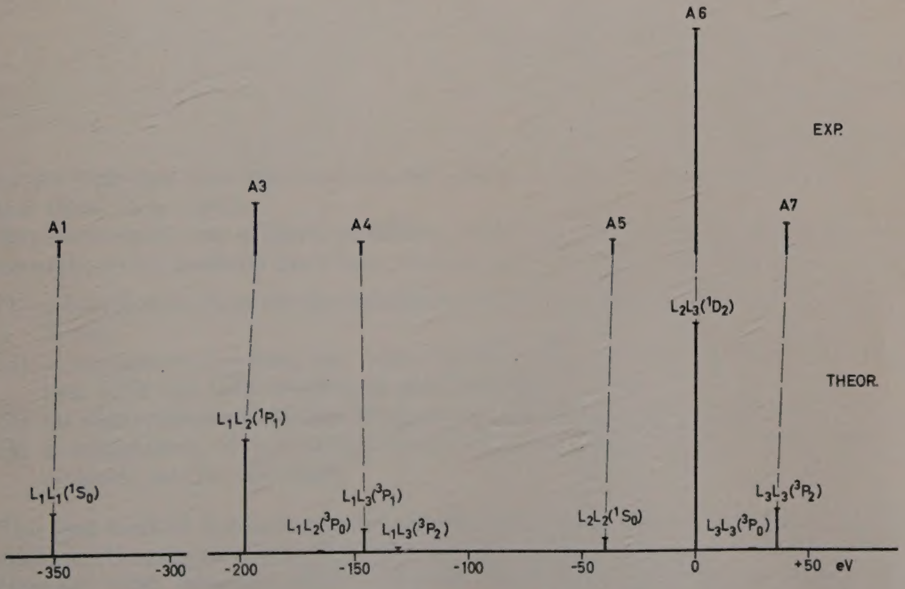

Fig. 3 *b*.

Fig. 3. Experimental and calculated [4] relative positions and intensities of the lines in the *KLL* Auger spectrum of (*a*) copper and (*b*) germanium. The theoretical lines have been normalized to the $L_{II}L_{III}(^1D_2)$ line and the experimental ones to the *A*6 line.

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Institute of Physics, University of Uppsala.

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